ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2015, **51**, 14921

Received 17th July 2015,
Accepted 14th August 2015

DOI: 10.1039/c5cc05969k

www.rsc.org/chemcomm

Two-dimensional covalent triazine framework as an ultrathin-film nanoporous membrane for desalination†

Li-Chiang Lin,‡[ab] Jongwon Choi‡[b] and Jeffrey C. Grossman*[b]

We computationally demonstrate that two-dimensional covalent triazine frameworks (CTFs) provide opportunities in water desalination. By varying the chemical building blocks, the pore structure, chemistry, and membrane performance can be designed, leading to two orders of magnitude higher water permeability than polyamide membranes while maintaining excellent ability to reject salts.

Water scarcity is one of the most prominent challenges in modern society.[1,2] Due to the rapid growth of the world population and the accelerated industrialization of developing countries, fresh water has become increasingly scarce. Although 75% of the earth's surface is covered with water, more than 97% of it is seawater that cannot be used directly. Much of the remaining fresh water is locked in glaciers and snowfields, leaving less than 1% of the world's water available for human consumption. Despite the vast availability of seawater, the production of fresh water using processes that separate salt ions from saline water (*i.e.*, desalination) remains negligible (less than 1%) when compared to global demand, primarily due to high costs and large energy consumption.[3]

To facilitate clean water production *via* desalination, much recent attention has been given to improving the cost-effectiveness and energy-efficiency of reverse osmosis (RO) desalination processes, which account for roughly two thirds of installed capacity. In particular, new membranes with enhanced water permeability compared to currently available polyamide-based membranes may have an important role to play in lowering energy consumption.[4] Several nanostructured materials have been previously investigated as promising membrane candidates such as carbon nanotubes (CNTs)[5–7] and zeolites.[8,9] Despite CNTs' high water permeability,[5] membranes based on CNTs exhibit poor salt rejection, and it remains challenging to fabricate membranes with dense, well-aligned nanotubes.[6,7] Zeolite membranes, on the other hand, possess three-dimensional networks that can effectively reject salt ions[8] but show relatively low water permeability.[9] Recently, nanoporous one-atom-thick graphene has drawn considerable attention and been shown computationally to provide significantly enhanced permeability compared to polyamide while maintaining excellent ability to reject salt.[10] Recent work of Surwade *et al.* has further experimentally realized such single-layered nanoporous graphene membranes and demonstrated their potential in desalination at the lab scale.[11] However, the production of nanoporous graphene membranes with perfectly sized nanopores still remains a great challenge. Moreover, to allow unprecedentedly high water fluxes, it is of great importance to achieve a pore density as high as possible while preventing pores from overlapping, a goal best achieved with a well-ordered pore structure. Seeking membranes with naturally ordered pores of an ideal size presents an important alternative to nanoporous graphene membranes.

Covalent organic frameworks (COFs), precisely ordered crystalline structures that were first reported by Yaghi and coworkers,[12] have drawn considerable attention in the scientific community due to their low density, large surface area, diverse functionality, and good thermal stability.[13–15] COFs are formed *via* self-assembly of precursor building blocks, and one can manipulate the structural topology by selecting different building blocks, leading to excellent structure tunability. COFs have been mostly studied as adsorbents for gas storage applications.[16,17] Given the need for highly controlled structures in membrane applications, it is surprising that the potential of COFs as membranes for water desalination has been largely overlooked. Similar to the case of one-atom-thick nanoporous graphene, single-layer two-dimensional COFs can also be synthesized.[18] Moreover, two-dimensional COFs possess precisely controlled and tunable nanoporous structures, making them a promising ultrathin-film membrane. The most widely investigated two-dimensional COFs to date are boron-containing structures such as the so-called COF-1.[12]

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[a] *Department of Process and Energy, Delft University of Technology, 2628 CB Delft, The Netherlands*

[b] *Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA. E-mail: jcg@mit.edu*

† Electronic supplementary information (ESI) available: Computational details, additional figures, and functionalized derivatives of the CTF-1 building block. See DOI: 10.1039/c5cc05969k

‡ These authors contributed equally to this work.

However, this class of COFs is unstable in the presence of water due to the reverse reaction of boronate ester or anhydride formation;[19] therefore boron-containing COFs are not good candidates for desalination. On the other hand, the two-dimensional covalent triazine COFs, so-called CTFs, display high chemical stability.[15] CTFs are ionothermally synthesized through a dynamic trimerization reaction, starting from cheap and abundant building blocks.[15,20]

Here we explore computationally the potential of two-dimensional CTFs as ultrathin-film membranes for desalination, employing classical molecular dynamics (MD) simulation techniques[21] as implemented within the LAMMPS package.[22] A Lennard-Jones (L-J) plus Columbic potential was used. The SPC/E[23] model was adopted for water molecules with the corresponding parameters proposed by Joung *et al.* for salt ions,[24] and L-J parameters from the Dreiding force field[25] for membrane atoms. The partial atomic charges of membrane atoms were derived using the REPEAT algorithm[26] based on an electrostatic potential calculated from density functional theory. CTF membranes were regarded as rigid. See ESI† for details.

We first studied single-layered CTF-0 and CTF-1 materials as membranes (see Fig. 1) for desalination.[20,27] Pore features including pore area and pore radius (*i.e.*, the largest free sphere radius) are analysed based on the van der Waals surface (see ESI† for details), with the key results summarized in Table 1. With a pore radius for CTF-0 of 0.56 Å, the pore of CTF-0 would be too small to allow passage of both water molecules and salt ions. Indeed, Fig. 2 and Table 1 show, as expected, that the water permeability of CTF-0 is zero while the salt rejection is 100%. The CTF-1 membrane, on the other hand, can have much bigger pores (*i.e.*, radius = 4.15 Å). From our calculations, we predict that the water permeability of CTF-1 can be as high as 64.2 L cm^{-2} day^{-1} MPa^{-1}, two to three orders of magnitude larger than currently available polyamide-based membranes.[28] Thanks to the porous nature of CTF materials, the pore density of CTF membranes is extremely high (*i.e.*, $\sim 5 \times 10^{13}$ pores per cm^2 for CTF-1) and this high density substantially facilitates water permeation through the membrane. As a comparison, the pore density of the nanoporous graphene membrane recently achieved experimentally is estimated to be $\sim 10^{12}$ pores per cm^2.[11] In addition, our calculations predict that the CTF-1 membrane is able to reject salt at a rate of 91%, which provides opportunities in brackish water desalination or multi-stage sea water desalination. This salt rejection rate, however, may not be high enough to meet the requirements of widely used one-step sea water RO processes (*i.e.*, nearly 100% is needed), indicating the membrane's pore is still marginally too large.

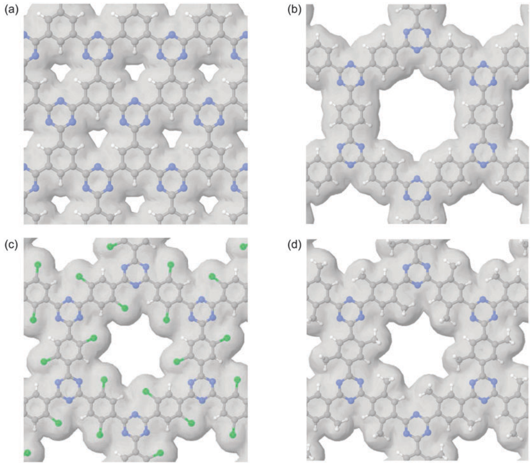

Fig. 1 Atomic structure and pore shapes. The atomic structure and pore shape of (a) CTF-0, (b) CTF-1, (c) CTF-1-Cl, and (d) CTF-1-CH_3. Colour code of grey: carbon, white: hydrogen, blue: nitrogen, and green: chlorine. van der Waals surfaces are shown in transparent grey.

Table 1 The desalination performance and structural properties of CTF membranes. The salt rejection in this work is defined as the percentage of salt ions remaining on the feed side when half of the feed water has permeated through the membrane at an applied pressure of approximately 53 MPa

Structure	Pore area ($Å^2$ $pore^{-1}$)	Pore radius (Å)	Water flux (L cm^{-2} day^{-1} MPa^{-1})	Salt rejection (%)
CTF-0	2.86	0.56	0.0	100
CTF-1	64.67	4.15	64.2 ± 5.1	91 ± 3
CTF-1-Cl	40.90	3.00	33.3 ± 3.5	96 ± 3
CTF-1-CH_3	41.99	2.99	24.6 ± 3.2	100

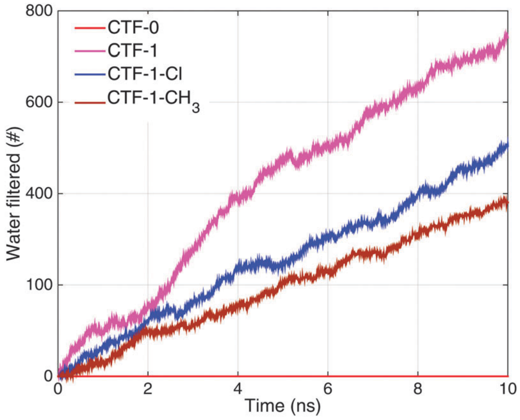

Fig. 2 Water molecules filtered. The number of water molecules filtered for different CTF membranes is shown as a function of simulation time. The result shown in this figure is from a single simulation.

As we discussed earlier, one of the promising properties of COF (or CTF) materials is their structural tunability, and one can thus further modify and design the pore structure by selecting different structural building units. In this case, we improve the salt rejection of the CTF-1 membrane by considering two different functionalized derivatives of the CTF-1 building block, CTF-1-Cl and CTF-1-CH_3. (See Fig. 1 for their atomic structures, both CTF-1-Cl and CTF-1-CH_3 structures adopted in this work were relaxed using the semi-empirical PM7 method.[29]) Table 1 clearly indicates that the pore size of both CTF-1-Cl and CTF-1-CH_3 has been effectively reduced compared to CTF-1. Our simulations show (Fig. 2 and Table 1) that the functionalization increases the ability of these two membranes to reject salt, and as expected there is a corresponding decrease in water permeability. The CTF-1-CH_3 and CTF-1-Cl membranes exhibit 100% and 96% salt rejection with a moderate water permeability decrease by roughly 60% and 50% compared to CTF-1, respectively. Since the structural characteristics of the pores in these two functionalized membranes are nearly identical as shown in Table 1, these results illustrate that the pore chemistry can also affect the membrane performance in desalination. The observed difference between these two membranes (*i.e.*, a lower salt rejection rate and higher permeability for CTF-1-Cl) is in agreement with the recent studies of nanoporous graphene, in which the hydroxylated nanoporous graphene membrane (*i.e.*, with negatively charged oxygen atoms of hydroxyl groups on the pore surface) was found to possess higher permeability but lower salt rejection compared to the hydrogenated one. Interestingly, it is also found that the negatively charged surface of CTF-1-Cl facilitates the passage of positively charged sodium ions as opposed to structures possessing a positively charged surface such as CTF-1 (see ESI†, Fig. S1 and S2). For each ion-pair passage (*i.e.*, Na^+ and Cl^-), the probability to have sodium ions passing through the membrane before chlorine ions is found to be approximately 71% and 14% for CTF-1-Cl and CTF-1, respectively. Finally, we note that many building blocks of such functionalized CTF-1 membranes have been synthesized and are commercially available (see ESI†, Fig. S3),[30] as in the case of CTF-1-CH_3.

Thus far we have shown that CTF membranes with properly chosen structural building blocks provide opportunities in water desalination. From a practical point of view, it remains crucial to understand the mechanical integrity of CTF membranes and the design of supporting substrates under the large hydraulic pressures of RO desalination processes.[31] In particular, we model the mechanical integrity of CTF-1 membranes against applied hydraulic RO pressure using the approach recently employed by Cohen-Tanugi *et al.*[32] MD simulations were used to estimate the intrinsic mechanical properties of CTF membranes including fracture stress, Young's modulus, and Poisson's ratio, whereas continuum fracture mechanics was used to determine the stress experienced by the CTF-1 membrane as a function of substrate pore radius at a macroscopic scale. In the MD simulations, we used reactive force fields (ReaxFF) with parameters from two different sets (*i.e.*, Budzien *et al.* and Strachan *et al.*)[33,34] to describe the chemical bonding of the CTF-1 framework. See ESI† for more details.

The stress–strain curve of CTF-1 membranes predicted from the biaxial strain test is shown in Fig. 3(a), and a consistent prediction was obtained using these two different sets of ReaxFF parameters. The results show that the fracture stress of CTF-1 can be as high as approximately 27 GPa at a critical strain of approximately 0.12. The corresponding Young's modulus is determined to be 200–220 GPa, depending on the adopted ReaxFF potential. The Young's modulus of the CTF-1 structure is in the same order of magnitude with that of COF-1 structures predicted from *ab initio* calculations, which has similar structural topologies but with different linker bonds.[35] Similarly, a consistent prediction was made in the uniaxial strain calculations, and a Poisson's ratio of approximately 0.85 was obtained. With these intrinsic material properties, we then determined the macroscopic stress experienced by the CTF membrane using a continuum mechanical model with a clamped boundary condition at the edge of substrate pores. Fig. 3(b) demonstrates the maximum applied pressure a CTF-1 membrane can withstand as a function of substrate pore radius, suggesting that a substrate with a pore size smaller than ~1.5 μm is needed to withstand a typical RO pressure of 5 MPa. A commonly used membrane supporting substrate, polysulfone, has a statistically averaged pore radius of 0.2 μm with a few or no pores larger than 2.5 μm.[36] Our analysis indicates that the mechanical strength of single-layered CTF-1 is sufficiently strong for the majority of substrate pores in polysulfone, although a chemical modification of the polysulfone structure may be needed to avoid outliers that possess large pore size in order to ensure the entire CTF-1 membrane maintains its mechanically integrity. It is, however, important to note that this class of materials is likely to intrinsically consist of multi-layers although single-layer structures have been synthesized. It has been shown that for 2D materials, such as graphene[37] and graphene oxide,[38] the Young's modulus remains approximately constant with an increased number of layers (*i.e.*, larger thickness). A multi-layered membrane will therefore experience smaller stress at a macroscopic scale compared to a single-layer one, leading to an improved mechanical integrity. Furthermore, such a multi-layered nature is not expected to change the effective pore size of the membranes since CTF-1, along with other derivatives of COFs, naturally forms AAA stacked structures, leading to vertically aligned pores.[15] As a comparison, in the case of nanoporous graphene that does not possess ordered pores, well-aligned pores between overlapping flakes may be extremely difficult to achieve.

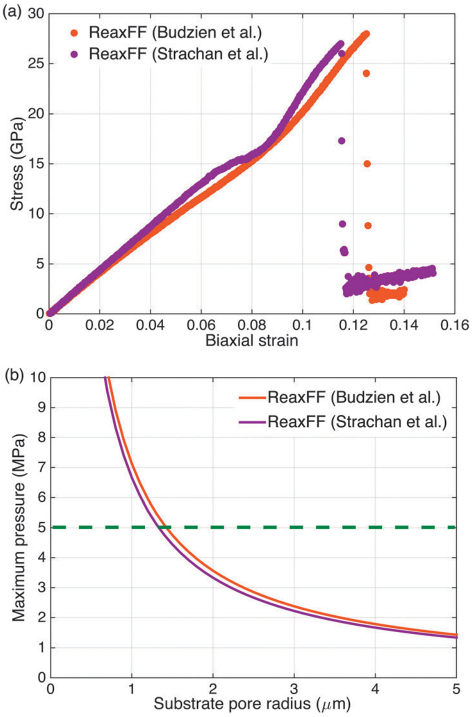

Fig. 3 Mechanical properties of CTF-1 membranes. (a) The biaxial stress–strain curve and (b) the maximum hydraulic pressure as a function of substrate pore radius. The dashed-green line shown in (b) represents a typical RO pressure of 5 MPa.

To date, the most studied approach to make ultrathin nanoporous membranes has been a top-down approach, *i.e.* create pores in an initially non-porous 2D material such as graphene. However, such an approach faces the challenge of accurately controlling the pore size with perfectly ordered pore structures. In this study, we propose two-dimensional covalent organic frameworks as candidates for ultrathin-film nanoporous membranes in RO desalination due to their precisely controlled and intrinsically ordered pore structure as well as excellent structural stability. Moreover, thanks to the tunable nature of this class of materials, this bottom-up approach offers straightforward control over the pore size and pore chemistry. Molecular dynamics simulations were employed to understand the potential of two-dimensional CTFs in water desalination. We show that a CTF membrane synthesized from a properly chosen building unit can achieve two to three orders of magnitude enhanced water permeability compared to currently available polyamide-based membranes and 100% salt rejection. The water permeability of CTF membranes and their ability to reject salt are substantially dominated by the pore size, although the pore chemistry also plays an important role. We note that the flexibility of the membrane, which is not considered in our model, may have a certain degree of influence on the predictions of desalination performance. For the case of nanoporous graphene, previous work showed this flexibility effect to be marginal,[39] although a direct correlation to CTF is not possible given its largely different chemical nature. Thermal fluctuations of the framework atoms and the deformation of structures under hydraulic pressure could lead to an effectively larger pore with a lower free energy barrier for transport. Accurately quantifying this effect on CTF membranes, however, is a complex problem and should include additional considerations such as the effects of multiple layers and the role of a support substrate. Such a detailed investigation will be the subject of future work. We have also used MD simulations to understand the mechanical properties of CTF membranes. The mechanical strength of single-layered CTF-1 membranes was found to be quite strong although a further chemical modification on a commonly used polysulfone supporting substrate or a multi-layered structure might be needed in order to avoid mechanical fracture. In summary, this work has demonstrated an alternative, promising approach to discover novel RO membranes using highly tunable COF/CTF materials. It is anticipated that our work can help guide the design of CTF materials as ultrathin-film nanoporous membranes for water desalination applications.

The research was supported by MIT Deshpande Center for Technology Innovation. This research used resources of the National Energy Research Scientific Computing Center (NERSC), a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This work was also supported by NWO Exacte Wetenschappen (Physical Sciences) for the use of supercomputer facilities, with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for Scientific Research, NWO).

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